

EFFECTS OF EXCHANGEABLE CATIONS ON THE CONVERSION OF LOW RANK COALS TO GASES AND LIQUIDS

Robert G. Jenkins

Fuel Science Program
Department of Materials Science and Engineering
The Pennsylvania State University, University Park, PA 16802

INTRODUCTION

It has become evident that for low rank coals (generally of subbituminous C and lower) the inorganic constituents play major roles in their utilization. These coals are partly characterized by the presence of significant quantities of carboxyl and phenolic groups which are, to varying degrees, associated with alkali and alkaline-earth metal cations (1,2,3,4). As an example, in an earlier study (2) we reported that these exchangeable metal cations can account for approximately 3 wt% (dmmf) of a Montana Lignite. The dominant exchangeable metal cation in US low rank coals is calcium. However, appreciable concentrations of sodium and magnesium are found (2,3). Generally, approximately between 30 to 60% of the carboxyl groups are associated with metal cations (2,3).

It is important to differentiate between these exchangeable inorganic species and the mineralogical components when considering the behavior of low rank coals under processing conditions. The most significant differentiation is, of course, their dispersion throughout the coal matrix. In the case of the exchangeable cations, they are dispersed on an atomic basis; that is, each metal cation is associated with one or two carboxylic acid groups. There have been many electron microprobe studies (5), for example, which have shown that the inorganic elements under investigation are extremely uniformly distributed through a lignite. In essence, in that type of study, it is impossible to resolve precisely the distribution because the cations are of an atomic size, much lower than the resolution of the instrument. When considering the mineralogical species, it is well established that the great majority of the minerals exist in size ranges greater than 1 μm . Thus, they are several orders of magnitude greater in size than the cations. This size differentiation has, of course, ramifications on the chemical behavior of the species as well as physical considerations. It is extremely likely that the exchangeable metal cations are of much different chemical reactivity than a like atom in the lattice of some mineralogical species. Finally, it must be realized that on pyrolysis (which accompanies combustion, gasification and liquefaction processes) that the carboxylic acid salts will decompose to liberate a metal cation as some chemically reactive entity. Even after some degree of sintering, or agglomeration, the cation derived species will be finely dispersed, i.e., still much smaller than the vast majority of mineralogical particles.

It is the goal of this presentation to review several recent studies which have shown the importance of understanding the nature of the exchangeable cations in the utilization of low rank coals.

DIRECT LIQUEFACTION

It is well known that during direct liquefaction there is always some amount of material which appears as insoluble, residual solids (6,7). These solids are composed of a wide range of carbonaceous and inorganic materials. However, in this case we are only interested in those generated during the liquefaction of low rank coals. The most important feature of reactor deposits obtained from these coals is the formation of calcium carbonate as calcite and/or metastable vaterite (6,7,8,9). Detailed optical and SEM studies on these solids indicates that carbonate is precipitated and is not related to calcite grains which may occur in the feed low

rank coal (6,7). The source of the calcium is the exchangeable calcium present in these coals. A semi-quantitative relationship can be found between the amount of deposited solids and the ion-exchangeable calcium content of the feed coal (6). Liquefaction experiments made on an acid washed coal resulted in no production of calcium carbonate. A series of experiments were made on a Wyodak subbituminous coal which was first demineralized and then back exchanged with calcium acetate solution. The calcium loaded (5 wt%), dried coal was then reacted at 400°C in tetralin (N₂, CO₂ and H₂S atmospheres) for periods varying from 10 to 60 min. The quantity of calcium carbonate was determined quantitatively by measuring the volume of CO₂ evolved on treating the reaction products with 1N HCl. The results of this series of experiments are shown in Figure 1. The data are expressed as a first-order plot in terms of the conversion of carboxylates to the theoretical amount of CaCO₃ that could be produced. It is obvious that these data fit the first order plot rather well. Under these conditions 50% of the exchangeable calcium is converted to carbonate after about 23 mins. The calculated rate constant is $5 \times 10^{-4} \text{ sec}^{-1}$. In all cases, the crystallographic form of calcium carbonate produced was found to be a mixture of calcite and vaterite. From the data plotted in Figure 1, it can be seen that the rate of conversion of calcium cations to carbonate, under these conditions, is not affected by the presence of the three gaseous atmospheres utilized (H₂O, N₂ and CO₂).

COAL PYROLYSIS

In any investigation dealing with the role of exchangeable metal cations in coal pyrolysis one has to be concerned with several gauges of pyrolysis behavior. As examples, it is important to gain understanding of the effects of the cations on total weight loss, tar evolution, product gas composition, decarboxylation and kinetics. Several investigations have been made into this general area. Tyler and Schafer (10), Franklin et al. (11), and Otake (12) studied the effects of exchangeable cations on total weight loss and tar yield over a wide range of reaction conditions. They found, in general, that replacement of the metal cations by protons leads to an increase in weight loss. Murray (14) and Schafer (15,16) studied the decarboxylation of low-rank coals in fixed-bed reactors at slow heating rates. They found that removing the metal cations does result in an increase in the amount of decarboxylation at any given temperature.

In recent studies in these laboratories (17,18,19), Morgan found profound effects of the metal cations on rapid pyrolysis of a Montana lignite in an entrained flow apparatus. Total weight loss, at 1173 K in N₂/He, was found to be a function of the presence of metal exchangeable cations for a residence time of about 250 ms (Table 1).

TABLE 1
EFFECT OF CATIONS ON MAXIMUM WEIGHT LOSS IN ENTRAINED
FLOW REACTOR, 1173 K, DICF* BASIS (17,18)

<u>Sample</u>	<u>mmoles cation/g DICF Coal</u>	<u>wt Loss</u>
Raw	0.94	31
Ca A	1.11	30
Ca B	0.84	29
Ca C	0.75	35
Ca D	0.49	39
Acid Washed	--	49

* DICF: Dry Inorganic Constituent Free

As can be seen from Table 1, as the loading of calcium increases there is a drop in the total yield. The most significant reductions takes place after the initial

loadings. After a certain level of calcium cations the effects become essentially constant. Morgan's studies also suggested that presence of exchangeable cations caused a reduction in the amount of tars evolved when compared to the acid-washed sample. FTIR spectra of the tars evolved in these cases indicated that tars from the raw coal contain three times the amount of aliphatic hydrogen as do the tars from the acid-washed sample. Finally, it was found that the presence of the metal cations retarded the decomposition of the carboxylic acid groups. In this study, the carboxylic acid concentrations were determined directly on the pyrolyzed lignite samples.

GASIFICATION REACTIVITY

It has been well recognized that the measured gasification reactivities of coal chars, prepared under similar conditions, are a function of the rank of the parent coal (20,21). The chars of highest reactivities are those derived from lignites. Correlation have been made between the reactivities and the amount of exchangeable calcium cations in the coals or calcium in the chars (20,21,22). However, it was not until the work of Radovic et al. (23,24,25,26,27) that it was shown, in the case of calcium loaded onto a North Dakota Lignite, the catalytic species was calcium oxide. In addition, it was established that the observation that reactivity was a function of the severity of pyrolysis conditions was due to catalyst crystallite growth (sintering). As pyrolysis severity increased then the measured reactivities were reduced. A correlation was drawn between the observed gasification reactivities and the dispersion (as measured by crystallite size) of the catalytically active calcium oxide. Thus, the gasification reactivity of lignite chars was shown to be dominated by the concentration of their inherent catalyst sites.

It is important to recognize that the aforementioned reactivity measurements have been made on chars and not the corresponding raw or pretreated lignites. It is becoming evident that the exchangeable cations can have significant effects on combustion and gasification of the coals themselves. Some data reported by Morgan and Jenkins (19) and Morgan and Scaroni (28) have indicated relationships between the presence/absence of exchangeable metal cation and the rates of gasification/combustion of lignites. It is apparent from their data that the effects of the cations on rapid pyrolysis rates can ultimately result in enhancements in oxidation reactivity.

SUMMARY

As research proceeds in the area of low rank coal utilization, it is becoming obvious that the inherent inorganic constituents of these coals have profound influences on their behavior. The reason for this influence is related to the fact that a significant proportion of the inorganic components are in the form of atomically dispersed exchangeable metal cations. It is evident that variations in the metal cation content can bring about significant differences in the performance and behavior of these coals. With that in mind, it may well be that we should be looking in more depth at the "beneficiation" of low rank coals by effecting alterations in the chemical distributions of the cations associated with their carboxylic acid functionalities.

ACKNOWLEDGEMENTS

The author would like to acknowledge all his colleagues with whom he has been associated. Financial support for the research studies were provided by the Gas Research Institute, Electric Power Research Institute, Department of Energy, and The Pennsylvania State University Cooperative Program in Coal Research.

REFERENCES

1. Schafer, H. N. S., Fuel 49, 197 (1970) and Fuel 49, 271 (1970).

2. Morgan, M. E., Jenkins, R. G., and Walker, P. L., Jr., Fuel 60, 189 (1980).
3. Bobman, M. H., Golden, T. C., and Jenkins, R. G., Solvent Extraction and Ion Exchange 1(4), 791 (1983).
4. Bobman, M. H., Golden, T. C., and Jenkins, R. G., Solvent Extraction and Ion Exchange 1(4), 813 (1983).
5. Fowkes, W. W., "Separation and Identification of Minerals from Lignites," Chapter 27, in Analytical Methods for Coal and Coal Products, Volume 2, Ed. C. Karr, Jr., Academic Press (1978).
6. Walker, P. L., Jr., Spackman, W., Given, P. H., Davis, A., Jenkins, R. G., and Painter, P. C., "Characterization of Mineral Matter in Coals and Coal Liquefaction Residues," Final Report to EPRI, AP-1634, November 1980.
7. Wakely, L. D., Davis, A., Jenkins, R. G., Mitchell, G. D., and Walker, P. L., Jr., Fuel 58, 379 (1979).
8. Brunson, R. J., Chabach, J. J., Chem. Geol. 25(4), 333 (1979).
9. Stone, J. B., Trachte, K. L., Poddar, S. K., Amer. Chem. Soc. (Fuel Chem. Div.) Preprints 24(2), 255 (1979).
10. Tyler, R. J. and Schafer, H. N. S., Fuel 59, 487 (1980).
11. Franklin, H. D., Cosway, R. G., Peters, W. A., and Howard, J. B., Ind. Eng. Chem. Process Des. Dev. 22, 39 (1983).
12. Otake, Y., M.S. Thesis, The Pennsylvania State University (1982).
13. Murray, J. B., Fuel 57, 605 (1978).
14. Schafer, H. N. S., Fuel 58, 667 (1979).
15. Schafer, H. N. S., Fuel 58, 673 (1979).
16. Morgan, M. E., Ph.D. Thesis, The Pennsylvania State University (1983).
17. Morgan, M. E., and Jenkins, R. G., Amer. Chem. Soc. (Fuel Chem. Div.) Preprints 28(4), 138 (1983).
18. Morgan, M. E., and Jenkins, R. G., Amer. Chem. Soc. (Fuel Chem. Div.) Preprints 29(2), 141 (1984).
19. Jenkins, R. G., Nandi, S. P., and Walker, P. L., Jr., Fuel 52, 288 (1973).
20. Hippo, E. J., and Walker, P. L., Jr., Fuel 54, 245 (1975).
21. Hippo, E. J., Jenkins, R. G., and Walker, P. L., Jr., Fuel 58, 338 (1979).
22. Radovic, L. R., Ph.D. Thesis, The Pennsylvania State University (1982).
23. Radovic, L. R., Walker, P. L., Jr., and Jenkins, R. G., Fuel 62, 209 (1983).
24. Radovic, L. R., Walker, P. L., Jr., and Jenkins, R. G., J. Catal. 82, 382 (1983).
25. Radovic, L. R., Walker, P. L., Jr., and Jenkins, R. G., Fuel 62, 849 (1983).

26. Radovic, L. R., Steczko, K., Walker, P. L., Jr., and Jenkins, R. G., submitted to Fuel.
27. Morgan, B. A., and Scaroni, A. W., Amer. Chem. Soc. (Fuel Chem. Div.) Preprints 28(4), 164 (1983).

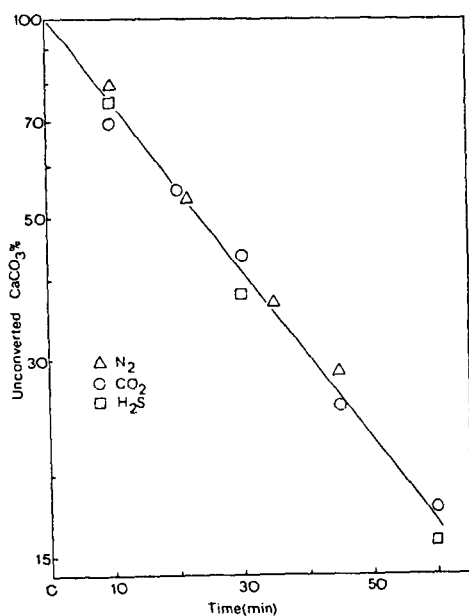


Figure 1. First Order Plot for Calcium Carbonate Formation at 400°C Under Pseudo-Liquefaction Conditions